

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2000-157870

(43)Date of publication of application : 13.06.2000

(51)Int.Cl.

B01J 29/12
B01D 53/94
B01J 29/44
F01N 3/10

(21)Application number : 11-338142

(71)Applicant : DEGUSSA HUELS AG

(22)Date of filing : 29.11.1999

(72)Inventor : KLEIN HARALD DR
STREHLAU WOLFGANG DR
LOX EGBERT
KREUZER THOMAS DR
MUELLER WILFRIED

(30)Priority

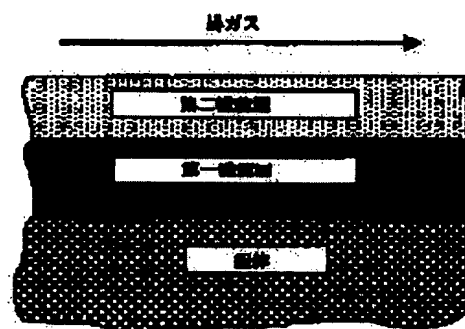
Priority number : 98 19854794 Priority date : 27.11.1998 Priority country : DE

(54) CATALYST FOR PURIFYING EXHAUST GAS FROM DIESEL ENGINE

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain the superior nitrogen oxide conversion rate on a continuous lean fuel-air mixture operation zone by additionally providing a second functional layer with hydrocarbon storage function for a catalyst having two functional layers consisting of a first layer of nitrogen oxide storage function and the second layer of catalyst function.

SOLUTION: A catalyst for converting a nitrogen oxide in an oxygen rich exhaust gas from a diesel engine under the optimum utilization of a reducing component contained in exhaust gas is provided with a second functional layer absorbing the catalyst activities and also hydrocarbon contained in a lean exhaust gas and formed



on a first functional layer of function of storing the nitrogen oxide. As an acidic carrier material for the catalyst activity component in the second functional layer, for example, aluminum silicate, silicon dioxide, titanium oxide or zirconium oxide can be used. The second functional layer contains aluminum-removed Y-zeolite, zeolite ZMS5, aluminumremoved mordenite or a mixture of them.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

Copyright (C); 1998,2003 Japan Patent Office

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号
特開2000-157870
(P2000-157870A)

(43) 公開日 平成12年6月13日 (2000. 6. 13)

(51) Int.Cl. ⁷	識別記号	F I	テマコード* (参考)
B 0 1 J 29/12	Z A B	B 0 1 J 29/12	Z A B A
B 0 1 D 53/94		29/44	A
B 0 1 J 29/44		F 0 1 N 3/10	A
F 0 1 N 3/10		B 0 1 D 53/36	1 0 4 B

審査請求 未請求 請求項の数15 O L (全 14 頁)

(21) 出願番号 特願平11-338142
(22) 出願日 平成11年11月29日 (1999. 11. 29)
(31) 優先権主張番号 1 9 8 5 4 7 9 4 . 3
(32) 優先日 平成10年11月27日 (1998. 11. 27)
(33) 優先権主張国 ドイツ (D E)

(71) 出願人 599020003
デグサーヒュルス アクチエンゲゼルシャ
フト
ドイツ連邦共和国、 フランクフルト、 ア
ム マイン ワイスフラウエンストラ
セ、 9
(72) 発明者 ハーラルト クライン
ドイツ連邦共和国 ベッセンバッハ オッ
トーザウアーシュトラッセ 17ア
(74) 代理人 100061815
弁理士 矢野 敏雄 (外3名)

最終頁に続く

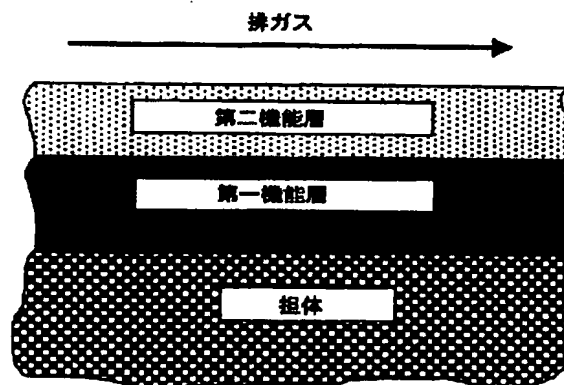
(54) 【発明の名称】 ディーゼルエンジンの排ガスの浄化のための触媒

(57) 【要約】

【課題】 排ガス中に含まれる還元性成分を窒素酸化物の還元を利用するディーゼルエンジンの連続浄化方法。

【解決手段】 窒素酸化物貯蔵を有する第一機能層および白金族金属による触媒機能を有し、かつ炭化水素貯蔵機能も有する第二機能層を用いる。

【効果】 連続したリーン混合気運転でも従来技術より高い窒素酸化物変換率が得られる。



【特許請求の範囲】

【請求項1】 第一の直接担体上にある層は窒素酸化物貯蔵機能を有し、かつ第二の直接排ガスと接触する層は触媒機能を有する、不活性担体上に2層に重なっている機能層を有するディーゼルエンジンの排ガスの浄化のための触媒において、第二機能層が追加的に炭化水素貯蔵機能を有し、かつその触媒機能は、高分散した形で微細な酸性担体材料上に沈着している白金族の触媒活性貴金属により提供されていることを特徴とする、ディーゼルエンジンの排ガスの浄化のための触媒。

【請求項2】 炭化水素貯蔵のための第二の機能層は、二酸化ケイ素の酸化アルミニウムに対するモル比20以上を有する酸性H-形にある少なくとも1種のゼオライト、ならびにその上に触媒活性成分として少なくとも1種の白金族貴金属が施用されている少なくとも1種の酸性担体材料を含む、請求項1記載の触媒。

【請求項3】 第二の機能層は、脱アルミニウムしたY-ゼオライト、ゼオライトZSM5または脱アルミニウムしたモルデン沸石またはこれらの混合物を含む、請求項2記載の触媒。

【請求項4】 酸性担体材料として、ケイ酸アルミニウム、二酸化ケイ素、酸化チタンまたは酸化ジルコニウムまたはこれらの混合物を使用し、これらの上に触媒活性成分として白金またはパラジウムまたはこれらの混合物を高分散の形で沈着させている、請求項3記載の触媒。

【請求項5】 酸性担体材料として、ケイ酸アルミニウムの全質量に対して二酸化ケイ素含有量1~10質量%を有するケイ酸アルミニウムを使用する、請求項4記載の触媒。

【請求項6】 窒素酸化物貯蔵のための第一機能層は、アルカリ金属、アルカリ土類金属および希土類金属の群からの少なくとも1種の窒素酸化物貯蔵化合物を含む、請求項1記載の触媒。

【請求項7】 第一機能層は、追加的にマンガン、コバルト、銅、亜鉛、スズ、鉛、ジルコニウムの群からの遷移金属の塩基性酸化物またはこれらの組合せを含む、請求項6記載の触媒。

【請求項8】 第一機能層内において、窒素酸化物貯蔵化合物は、高分散の形で、1種またはそれ以上の担体材料上に存在する、請求項6記載の触媒。

【請求項9】 第一機能層内において、窒素酸化物貯蔵化合物のための少なくとも1種の担体材料は、酸化セリウムを基とする担体材料である、請求項7記載の触媒。

【請求項10】 酸化セリウムを基とする担体材料は、酸化セリウムまたは混合酸化物の全質量に対するジルコニウム含有量1~30質量%を有するセリウム/ジルコニウム混合酸化物である、請求項8記載の触媒。

【請求項11】 第一機能層は、追加的に白金族からの少なくとも1種の触媒活性貴金属を含む、請求項1記載の触媒。

(2)

特開2000-157870

2

【請求項12】 両方の機能層は、総濃度100~400g/lにおいて担体上に存在する、請求項1記載の触媒。

【請求項13】 第二機能層の質量割合が、全被覆物の10~50質量%となっている、請求項10記載の触媒。

【請求項14】 エンジンの大部分の運転の間に空気過剰率1以上を有するディーゼルエンジンの排ガスの浄化のための方法において、排ガス温度がエンジンの大部分の運転時間の間に400℃以下にある排ガス装置のある場所に配置されている請求項1~11記載の何れか1項記載の触媒に排ガスを導通させることを特徴とする、ディーゼルエンジンの排ガスの浄化のための方法。

【請求項15】 触媒担体の幾何学的表面積対ディーゼルエンジンの気筒容積の比が1~10m²/lである、請求項12記載の方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、ディーゼルエンジンの排ガスの浄化のための触媒に関する。本発明による触媒を用いて、ディーゼルエンジンの酸素リッチ排ガス中の窒素酸化物を、排ガス中に含まれる還元性成分の最適な利用の下に変換できる。

【0002】

【従来の技術】ディーゼルエンジンは、利用されなかった酸素および無害な燃焼生成物、例えば水および二酸化炭素の他に、追加して人間の健康を損ないかつ環境に負荷となる有害物質を含む排ガスを放出する。これには、一酸化炭素CO、未燃炭化水素HC、窒素酸化物NO_xおよび粒子状物質が属する。窒素酸化物は、燃焼の間に燃焼空気の窒素から形成されるか、または燃料中の窒素含有化合物から生成する。これらは、エンジンの作動点に従って、約50~90容積%が一酸化窒素NOから成る。さらに、内燃機関の排ガスは、燃料の硫黄含有量に応じてさらに二酸化硫黄を含む。

【0003】空気の清浄維持のために、これらの有害物質の排出に対して規定されている上限値が行政者により規定された。限界値は、技術的な可能性に従って、有害物質排出を減少させるために時に応じて下方に修正される。排ガス浄化システムの有害物質変換の実際に近似させた試験のために、各種の試験サイクルが規定され、これらは頻繁に現れる運転条件にシミュレーションされている。

【0004】ヨーロッパにおいて現行の車両の試験サイクルは、MVEG-Aサイクル（自動車両排出物グループ）と呼ばれ、市街地運転期間（ECE）および市街地外運転期間（EUDC）部分から成る。これによると、検査する車両は、ローラ試験台（Rollenprüfstand）上で相当する運転サイクルを走行する。ローラ試験台の遠心質量フライホイールは、集中負荷を構成し、かつ車両の

質量をシミュレーションする。運転サイクルの間に、排出される気体状有害物質は、標準分析方法〔HC：水素炎イオン化形検出器（FID）、CO：赤外分光分析器（IR）、NO_x：化学蛍光検出器（CLD）〕により測定、積算され、全サイクルの有害物質排出量をg（有害物質）／走行kmで表される。これらの排出量は法規に規定された限界値と比較できる。

【0005】その排ガス組成に応じて、今日の内燃機関は、二種類に分類できる。その一つには、通常のオートエンジンがあり、その排ガスは実質的に化学量論組成であり、また他方はディーゼルエンジンおよびリーン（希薄混合気燃焼）運転オートエンジンであり、これらの排ガスは酸素を過剰に含んでいる。

【0006】通常のオートエンジンの排ガスは、上記の有害物質の他に、さらに酸素含有量約0.7容積%を有する。これは化学量論的に構成されたものであり、すなわち、排ガスの酸化性と還元性成分とが均衡し、またいわゆる三元触媒を用いて同時にかつほとんど完全に無害な成分の二酸化炭素、水および窒素に変換できる。三元触媒は、高表面積担持酸化物上に触媒として活性成分として白金および／またはパラジウムの他にロジウムも含み、これらは、殊に還元剤として一酸化炭素および未燃炭化水素を用いて窒素酸化物の窒素への選択的還元を促進する。三元触媒による三種の有害物質の同時変換のための前提条件は、エンジンに導かれる空燃比を化学量論値に制御することである。これは、慣用の燃料の場合に14.6である。すなわち、空気14.6kgが燃料1kgの完全燃焼に必要とされる。

【0007】これに反して、ディーゼルエンジンおよびリーン運転オートエンジンの排ガスは、約6~20容積%の高い酸素含有量を有し、それというのもこれらのエンジンはリーンな空燃比を用いて運転されるからである。これらのエンジンの場合の大きい問題は、窒素酸化物の排出である。排ガスの高い酸素含有量のために、窒素酸化物を従来の三元触媒により、還元剤として一酸化炭素および炭化水素を用いて変換することは不可能である。さらに、一酸化炭素および炭化水素の酸化が、酸素含有量の高い排ガス中では優先する。

【0008】従ってしばしば、これらのエンジンの排ガスは、いわゆる酸化触媒を用いてのみ酸化的に浄化され、すなわち、一酸化炭素および炭化水素は触媒において排ガス中の酸素により水および二酸化炭素に酸化される。このような触媒は、例えばドイツ特許（DE）第3940758C1号明細書中に記載されている。これは、一酸化炭素および炭化水素の酸化のための高い触媒活性を特徴とし、一方では一酸化窒素の二酸化窒素へ、および二酸化硫黄の三酸化硫黄への逐次酸化は十分に抑制される。これにより、使用される触媒を被毒することがある硫酸塩の形成も低下する。この触媒は、高表面積担持酸化物、例えば酸化アルミニウム、酸化チタンおよ

び二酸化ケイ素の上に、触媒活性成分として白金および／またはパラジウムを含み、これらは酸化バナジウムの添加により、一酸化窒素および二酸化硫黄の逐次酸化がほとんど認められないようにその触媒活性を変性するという特徴を有する。

【0009】これらのエンジンの排ガス中の窒素酸化物の低下のために、種々の解決法がある。いわゆる選択的触媒還元法（SCR：Selective Catalytic Reduction）は、排ガス中の窒素酸化物をSCR触媒において排ガスに還元剤を加えることにより選択的に還元させる。還元剤として、燃料自体を用いることもできる。最適な結果は、還元剤としてアンモニアを用いて到達され、これは、例えば車両上で尿素の加水分解により製造できる。このような方法は、ドイツ特許（DE）第4203807A1号明細書中に記載されている。好適なSCR触媒は、欧州特許（EP）第0410440B1号明細書中に記載されている。これは、チタン、鉄、バナジウム、モリブデン、タングステンの酸化物および種々のその他の添加剤の緊密な混合物から成る。

【0010】選択的触媒還元は、工業的には、貨物自動車内の大型ディーゼルエンジンの場合にのみ使用できる。従って、リーン運転オートエンジンの排ガス内の窒素酸化物の還元のために、近年において、いわゆる窒素酸化物貯蔵触媒の使用が提案された。この方法では、窒素酸化物は、貯蔵触媒において白金族金属により二酸化窒素に酸化され、かつ塩基性貯蔵材料により硝酸塩の形で貯蔵される。触媒の貯蔵能力を使い尽くした後にこれを再生しなければならない。再生は、エンジン運転をリーンな空気／燃料混合物からリッチ（濃厚混合気燃焼）、すなわち還元性の空気／燃料混合物に切り換えて開始する。還元性排ガス雰囲気中で、貯蔵から放出された硝酸塩は、窒素酸化物を遊離して分解し、これは還元性排ガス条件下で白金族金属において窒素に変換される。このように、この方法の場合には、SCR法と同様に追加の燃料の形の活性還元剤が使用される。このために、定期的にリーン運転からリッチ運転への切り換えに適するエンジン電子系が必要である。

【0011】欧州特許（EP）第0669157A1号明細書は、このような方法を記載している。窒素酸化物のための貯蔵触媒として、塩基性材料、例えばアルカリ金属酸化物、アルカリ土類金属酸化物および希土類元素酸化物が使用される。追加的に、貯蔵触媒は、高表面積担持酸化物上の白金および／またはパラジウムを含む。

【0012】排ガス浄化の改善のためおよび耐硫黄性の向上のために、貯蔵触媒と他の触媒との種々の組合せが公知となっている。すなわち、欧州特許（EP）第0716876A1号明細書は、担体上に二種の多孔性担体層を有する触媒を記載している。第一の担体層は、窒素酸化物のための貯蔵材料としてのバリウムならびにパラジウムを含む。第二の担体層は第一の担体層の上に置か

*** NOTICES ***

JPO and NCIP are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] The layer which the layer on the first direct support has a nitrogen-oxides storage function, and contacts the second direct exhaust gas has a catalyst function. In the catalyst for clarification of the exhaust gas of the diesel power plant which has the stratum functionale which has lapped on the inert carrier two-layer It is a catalyst for clarification of the exhaust gas of a diesel power plant which the second stratum functionale has a hydrocarbon storage function additionally, and is characterized by offering the catalyst function with the catalytic activity noble metals of the platinum group which is carrying out deposition on the acid detailed support ingredient in the form which carried out high distribution.

[Claim 2] The second stratum functionale for hydrocarbon storage is a catalyst containing at least one sort of zeolites in acid H-form where it has 20 or more mole ratios to the aluminum oxide of a silicon dioxide, and at least one sort of acid support ingredients, with which at least one sort of platinum group noble metals are used as a catalytic activity component on it according to claim 1.

[Claim 3] The second stratum functionale is a catalyst containing Y-zeolite which carried out dealuminization, a zeolite ZSM5, the mordenites which carried out dealuminization, or such mixture according to claim 2.

[Claim 4] The catalyst according to claim 3 which an aluminum silicate, a silicon dioxide, titanium oxide, zirconium dioxides, or such mixture are used [catalyst], and carries out the deposition of platinum, palladium, or such mixture in the form of high distribution as a catalytic activity component on these as an acid support ingredient.

[Claim 5] The catalyst according to claim 4 which uses the aluminum silicate which has the silicon-dioxide content 1 - 10 mass % to the total mass of an aluminum silicate as an acid support ingredient.

[Claim 6] The primary-function layer for nitrogen-oxides storage is a catalyst containing at least one sort of nitrogen-oxides storage compounds from the group of alkali metal, alkaline earth metal, and a rare earth metal according to claim 1.

[Claim 7] A primary-function layer is a catalyst according to claim 6 which includes the basic oxides or these combination of transition metals from a group of manganese, cobalt, copper, zinc, tin, lead, and a zirconium additionally.

[Claim 8] It is the catalyst according to claim 6 to which a nitrogen-oxides storage compound

exists on one sort or the support ingredient beyond it in the form of high distribution in a primary-function layer.

[Claim 9] It is the catalyst according to claim 7 at least one sort of whose support ingredients for a nitrogen-oxides storage compound are support ingredients based on cerium oxide in a primary-function layer.

[Claim 10] The support ingredient based on cerium oxide is a catalyst according to claim 8 which are the cerium / zirconium mixed oxide which has the zirconium content 1 - 30 mass % to the total mass of cerium oxide or a mixed oxide.

[Claim 11] A primary-function layer is a catalyst according to claim 1 which contains at least one sort of catalytic activity noble metals from a platinum group additionally.

[Claim 12] Both stratum functionale is catalysts according to claim 1 which exist on support in the total concentration 100 - 400 g/l.

[Claim 13] The catalyst according to claim 10 from which the mass rate of the second stratum functionale is 10 - 50 mass % of all coatings.

[Claim 14] The approach for clarification of the exhaust gas of a diesel power plant characterized by the thing which is arranged in the location which has exhaust gas equipment which has exhaust gas temperature in 400 degrees C or less between operation time engine [most] in the approach for clarification of the exhaust gas of the diesel power plant which has one or more excess air factors between operations engine [most], and which make a catalyst given [according to claim 1 to 11] in any 1 term flow through exhaust gas.

[Claim 15] The approach according to claim 12 the ratio of the cubic capacity of the geometric surface area pair diesel power plant of catalyst support is 1-10m²/l.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the catalyst for clarification of the exhaust gas of a diesel power plant. The nitrogen oxides in the oxygen rich exhaust gas of a diesel power plant are convertible for the bottom of the optimal utilization of the reducibility component contained in exhaust gas using the catalyst by this invention.

[0002]

[Description of the Prior Art] A diesel power plant emits the exhaust gas containing the harmful matter which ruins its health of human being in addition besides the oxygen which was not used, harmless products of combustion, for example, water, and a carbon dioxide, and serves as a load at an environment. A carbon monoxide CO, unburnt hydrocarbon HC, nitrogen oxides NO_x, and particulate matter belong to this. Nitrogen oxides are formed from the nitrogen of a combustion air between combustion, or are generated from the nitrogen content compound in a fuel. According to an engine working point, as for these, about 50 to 90 volume % consists of a nitrogen monoxide NO. Furthermore, an internal combustion engine's exhaust gas contains a sulfur dioxide further according to the sulfur content of a fuel.

[0003] The upper limit specified to blowdown of such harmful matter for clarification maintenance of air was specified by the administration person. According to technical possibility, by the way, threshold value is caudad corrected, in order to decrease harmful matter blowdown.

Various kinds of trial cycles are specified for the trial made to approximate actually [harmful matter conversion of an emission-gas-purification system], and simulation of these is carried out to the service condition which appears frequently.

[0004] In Europe, the trial cycle of the present car is called a MVEG-A cycle (motor vehicle excretions group), and consists of an urban area operating period (ECE) and the operating-period (EUDC) part outside an urban area. According to this, the car to inspect runs the run cycle which corresponds on the roller test board (Rollenpruefstand). The centrifugal mass flywheel of the roller test board constitutes a concentration load, and carries out simulation of the mass of a car. The gas-like harmful matter discharged between run cycles is a standard analysis approach [HC:hydrogen flame ionization form detector (FID), CO:infrared-spectroscopic-analysis machine (IR), and NOx. : It is measured and integrated by chemistry fluorescence detector (CLD)] and express the harmful matter discharge of a complete cycle with g (harmful matter) / transit km. These discharges can be measured with the threshold value specified to the regulation.

[0005] Today's internal combustion engine can classify into two kinds according to the exhaust gas presentation. There is the usual Otto engine, the exhaust gas is stoichiometric composition substantially, and another side is a diesel power plant and a Lean (lean-mixture combustion) operation Otto engine, and these exhaust gas contains oxygen in one of them superfluously.

[0006] The exhaust gas of the usual Otto engine has oxygen content about 0.7 volume % other than the above-mentioned harmful matter further. It is constituted by stoichiometric, the oxidizing quality and reducibility component of exhaust gas are balanced, and this can be changed into the carbon dioxide, water, and nitrogen of a simultaneous and almost completely harmless component using the so-called three way component catalyst. In a three way component catalyst, these other than platinum and/or palladium promote [on high surface area support oxide] the alternative reduction to the nitrogen of nitrogen oxides especially also including a rhodium as an active ingredient as a catalyst, using a carbon monoxide and unburnt hydrocarbon as a reducing agent. The prerequisite for simultaneous conversion of three sorts of harmful matter by the three way component catalyst is controlling the air-fuel ratio led to an engine to a stoichiometry value. In the case of the fuel of common use, this is 14.6. That is, 14.6kg of air is needed for the perfect combustion which is 1kg of fuels.

[0007] In contrast, the exhaust gas of a diesel power plant and a Lean operation Otto engine is because it has the high oxygen content of about six to 20 volume % and they, that is, these engines are operated using a Lean air-fuel ratio. The large problem in the case of these engines is blowdown of nitrogen oxides. It is impossible to use a carbon monoxide and a hydrocarbon and to change nitrogen oxides as a reducing agent, with the conventional three way component catalyst for the high oxygen content of exhaust gas. Furthermore, oxidation of a carbon monoxide and a hydrocarbon has priority in exhaust gas with a high oxygen content.

[0008] Therefore, only by using the so-called oxidation catalyst for the exhaust gas of these engines, it is purified in oxidation, namely, a carbon monoxide and a hydrocarbon often oxidize to water and a carbon dioxide by the oxygen in exhaust gas in a catalyst. Such a catalyst is indicated for example, in the 3940758th patent (DE) C No. 1 description of Germany. This is characterized by the high catalytic activity for oxidation of a carbon monoxide and a hydrocarbon, and, on the other hand, the serial oxidation to the nitrogen dioxide of a nitrogen monoxide and the sulfur trioxide of a sulfur dioxide is fully controlled. Formation of the sulfate which may carry out poisoning of the catalyst used by this also falls. As for this catalyst, these have the description of a nitrogen monoxide and a sulfur dioxide of denaturalizing that catalytic

activity so that oxidation may hardly be accepted serially, by addition of a vanadium oxide including platinum and/or palladium as a catalytic activity component on high surface area support oxide, for example, an aluminum oxide, titanium oxide, and a silicon dioxide.

[0009] There is various solution for lowering of the nitrogen oxides in the exhaust gas of these engines. The so-called alternative catalytic reduction method (SCR: Selective Catalytic Reduction) makes the nitrogen oxides in exhaust gas return selectively by adding a reducing agent to exhaust gas in an SCR catalyst. The fuel itself can also be used as a reducing agent. The optimal result reaches using ammonia as a reducing agent, and this can be manufactured by hydrolysis of a urea for example, on a car. Such an approach is indicated in the German (patent DE) No. 4203807A1 description. The suitable SCR catalyst is indicated in the Europe (patent EP) No. 0410440B1 description. This consists of the oxide of titanium, iron, vanadium, molybdenum, and a tungsten, and the close mixture of the additive of various others.

[0010] Industrially, only in the case of a large-sized diesel power plant cargo automatic in the car, alternative catalytic reduction can be used. Therefore, in recent years, the so-called activity of a nitrogen-oxides storage catalyst was proposed for reduction of the nitrogen oxides in the exhaust gas of a Lean operation Otto engine. In this approach, nitrogen oxides oxidize to a nitrogen dioxide with a platinum metal in a storage catalyst, and are stored in the form of a nitrate with a basic storage ingredient. This must be reproduced after using up the storage capacity of a catalyst. Playback switches engine operation from Lean air / fuel mixture to rich (rich mixture combustion), i.e., the air / fuel mixture of reducibility, and begins. In a reducibility exhaust gas ambient atmosphere, the nitrate emitted from storage separates and disassembles nitrogen oxides, and this is changed into nitrogen in a platinum metal under reducibility exhaust gas conditions. Thus, in the case of this approach, the activity reducing agent of the form of an additional fuel is used like the SCR method. For this reason, the engine electronic system which is periodically suitable for the switch to rich operation from Lean operation is required.

[0011] The Europe (patent EP) No. 0669157A1 description has indicated such an approach. As a storage catalyst for nitrogen oxides, a basic ingredient, for example, an alkali-metal oxide, an alkaline-earth-metal oxide, and a rare-earth-elements oxide are used. Additionally, a storage catalyst contains the platinum and/or palladium on high surface area support oxide.

[0012] Because of [for an improvement of emission gas purification] improvement in sulfur-proof nature, the various combination of a storage catalyst and other catalysts is well-known. That is, the Europe (patent EP) No. 0716876A1 description has indicated the catalyst which has two sorts of porous support layers on support. The first support layer contains the barium and palladium as a storage ingredient for nitrogen oxides. The second support layer is placed on the first support layer, and including platinum, this oxidizes the nitrogen monoxide in Lean exhaust gas to a nitrogen dioxide, and, thereby, improves destorage of the nitrogen oxides by the first pass. In stoichiometric composition or rich exhaust gas, desorption of the nitrogen oxides stored in the first pass is carried out, and it returns to element-like nitrogen with palladium and platinum. The palladium in the first pass protects a storage ingredient from poisoning by the sulfur dioxide. As a support ingredient for the first and the second support layer, the Europe (patent EP) No. 0716876A1 description mentions an aluminum oxide, a silicon dioxide, an aluminum silicate, titanium oxide, and the analogue. Advantageously, an aluminum oxide is used as a support ingredient to both support layers.

[0013] Similarly, the Europe (patent EP) No. 0664147A2 description has indicated the catalyst which has the third catalyst which consists of the noble metals on the first catalyst which changes

from the noble metals on a porous and acid support ingredient to the flow direction of exhaust gas at the beginning, the second catalyst which consists of the storage ingredient to nitrogen oxides, and a porous support ingredient for an improvement of the sulfur resistance of a storage ingredient. The sulfur dioxide contained in Lean exhaust gas receives neither adsorption nor oxidation from the first catalyst, therefore the second catalyst can be passed, without forming a sulfate. In the exhaust gas of stoichiometric composition, rich or the stored nitrogen oxides is isolated from the second catalyst, and is returned to element-like nitrogen in the third catalyst. As a support ingredient porous [for the first catalyst], and acid, SiO₂, ZrO₂, SiO₂-aluminum 2O₃, and TiO₂ are proposed.

[0014] WO97/02886 description has indicated the constituent for conversion of the nitrogen oxides in exhaust gas which approach and contain the catalyst and nitrogen-oxides adsorption ingredient for conversion of nitrogen oxides. The catalyst for conversion of nitrogen oxides has a high distribution platinum metal component on the first support ingredient. The ingredient which adsorbs nitrogen oxides contains a separated basic metallic oxide with a platinum metal component. In an advantageous embodiment, the catalyst for conversion of nitrogen oxides is used on support in the form of the first enveloping layer. The ingredient which adsorbs nitrogen oxides is used on the first enveloping layer in the form of the second enveloping layer in this case. Both layers are mutually exchangeable. As a storage compound, the metallic oxide, the metal hydroxide, the metal carbonate, and the metal mixed oxide are indicated. A metal may be a lithium, sodium, a potassium, a rubidium, caesium, magnesium, calcium, strontium, or barium. in order to protect the ingredient which adsorbs nitrogen oxides from poisoning with sulfur -- a sulfur adsorbent component -- cerium oxide may be included advantageously. In the form of a particle, even if this cerium oxide exists in the particle side of a storage ingredient, it may be distributed in a nitrogen-oxides storage compound.

[0015] For clearance of the nitrogen oxides from exhaust gas using the catalyst array by WO97/02886 description, periodically, from Lean, the presentation of exhaust gas is controlled in a theoretical-value row corresponding to an air-fuel ratio, and is richly, switched to it up and down.

[0016] WO97/43031 description has proposed the approach for clearance of the nitrogen oxides from the exhaust gas from a diesel power plant especially. According to this, exhaust gas is first drawn on a nitrogen-oxides reduction catalyst succeeding on a nitrogen-oxides storage object. A nitrogen-oxides storage object includes the combination which consists of an oxidation catalyst and a storage ingredient. In order to carry out desorption of the adsorbed nitrogen oxides thermally in front of a nitrogen-oxides storage object, ** ON of the hydrocarbon is periodically carried out into exhaust gas. Even if it does not take another means, it leads to the average nitrogen-oxides conversion rate 0 now. Therefore, additionally, in order to obtain true conversion of nitrogen oxides, ** ON of the hydrocarbon must be anew carried out into exhaust gas in front of a reduction catalyst.

[0017] According to WO97/43031 description, the hydrocarbon by which ** ON was carried out in front of the nitrogen-oxides storage object burns in the oxidation catalyst of a nitrogen-oxides storage object. Although these determine that it is maintained by the amount as the presentation of exhaust gas is Lean, however in order that the heat generated in the case of the combustion in a nitrogen-oxides storage object may carry out desorption of the stored nitrogen oxides thermally, they are enough.

[0018] Thus, the well-known approach for operation of a storage catalyst always requires

periodic lifting of the hydrocarbon content of exhaust gas for the stored nitrogen oxides, rich or in order to decompose under the exhaust gas conditions of the amount of theory or to carry out desorption thermally in a storage catalyst by the temperature rise. Whether it is based on lowering of the air-fuel ratio introduced into an engine or it is based on the ** ON of the fuel into exhaust gas equipment after an engine perform lifting of the hydrocarbon content of exhaust gas in that case.

[0019] These active approaches for nitrogen-oxides blowdown reduction of a Lean operation engine are unsuitable to utilization to a diesel power plant, as long as these need rich-ization of air / fuel mixture, and they are because it operates rightly only by it, that is, these using fixed Lean air / fuel mixture. An active approach is based on rich-ization of air / fuel mixture, or is led to higher fuel consumption by injection of the fuel into exhaust gas.

[0020] Probably, high fuel consumption is especially avoidable by the diesel power plant, since it has nitrogen oxide emissions with a comparatively low diesel power plant. That is, the unburnt hydrocarbon, the carbon monoxide, and hydrogen which are still contained in the exhaust gas of a diesel power plant serve as a reducing agent of amount sufficient on the average in order to fully reduce little nitrogen-oxides blowdown.

[0021] Therefore, improving rich-ization of exhaust gas only using the reducibility component contained anyway in exhaust gas without falling nitrogen oxides in the case of a diesel power plant is also studied. For this reason, the suitable catalyst is indicated in the German (patent DE) No. 19614540 description. The conversion rate obtained by this for direct oxidation of the reducibility component which occurs simultaneously by high oxygen content of exhaust gas since it is the low selectivity of nitrogen-oxides reduction is low. In the case of the rate of the equal and high hydrocarbon under optimum conditions (i.e., the inside of exhaust gas), it reaches at 60% of conversion rates. However, if the so-called trial cycle MVEG-A is used, with such a catalyst, about 14% of conversion rates will be obtained.

[0022]

[Problem(s) to be Solved by the Invention] Therefore, the technical problem of this invention is enabling the most effective possible utilization of the reducibility component contained in exhaust gas for reduction of nitrogen oxides, and offering the catalyst for clarification of the continuous Lean exhaust gas of the diesel power plant led to the nitrogen-oxides reduction averaged through the run cycle which is higher than a well-known reduction catalyst, and appears in practice by the approach of a parenthesis.

[0023]

[Means for Solving the Problem] The layer which the layer which this technical problem has on the first direct support has a nitrogen-oxides storage function, and contacts the second direct exhaust gas is solved by the catalyst for clarification of the exhaust gas of the diesel power plant which has the stratum functionale which has lapped on the inert carrier two-layer which has a catalyst function. As for this catalyst, the second stratum functionale has a hydrocarbon storage function additionally, and it is characterized by offering that catalyst function with the catalytic activity noble metals of the platinum group which is carrying out deposition on the acid detailed support ingredient in the form which carried out high distribution.

[0024] As stratum functionale, the exhaust gas to pass considers the distributed enveloping layer on an inert carrier which can change the chemical presentation within the limits of this invention. The change can consist of removing a regular exhaust gas component from exhaust gas temporarily at least by adsorption for the component of the stratum functionale. In this case, the

storage ingredient for the nitrogen oxides which can store nitrogen oxides in the form of a nitrate from exhaust gas is well-known. Similarly, the zeolite for storage of the hydrocarbon contained in exhaust gas is also well-known.

[0025] It has passing another influence of the chemical composition of exhaust gas on transforming regular harmful matter to a product harmless in the case of contact for the component of the stratum functionale using other components of exhaust gas. The deposition of this catalyst function is advantageously carried out for these on a detailed support ingredient in the form of the high distribution for the noble metals of a platinum group, and the exertion with that catalytic activity it is especially brought from *****, palladium, a rhodium, and iridium, and perfect. The catalytic activity can change with the so-called addition of a co-catalyst. In many cases, this is the compound of base metal.

[0026] For a classification of the type of catalytic activity, it is often called an oxidation catalyst, a reduction catalyst, or a three way component catalyst. However, three sorts of these catalyst functions are mutually inseparable uniquely. It is related also to the presentation of exhaust gas whether the presentation of the given stratum functionale is excellent in which function at the actual target. In this case, a three way component catalyst can change a carbon monoxide, a hydrocarbon, and nitrogen oxides simultaneously, only when exhaust gas is stoichiometric composition. In order for the so-called reduction catalyst to be able to demonstrate the reduction activity, exhaust gas must contain sufficient reduction component, i.e., a carbon monoxide, a hydrocarbon, and hydrogen. Thereby, a reduction component oxidizes.

[0027] The thing of the powdered ingredient which remains as it is and is introduced in a catalyst within the limits of this invention as a detailed ingredient is considered. For that, in the patent specification indicated in English, the expression of "a bulk material (bulk material)" or "a particle-like ingredient (particulate material)" is used. These ingredients are often used as a support ingredient for the catalytic activity component of a catalyst, or other high variance components. For this object, a support ingredient must have a specific surface area (it is also called BET surface area, for example, measured by DIN66132) high for acceptance of these components. Within the limits of this invention, when the specific surface area exceeds 10m²/g, a detailed ingredient is called high surface area.

[0028] A detailed ingredient and a high distribution ingredient are distinguished. By impregnation, a high distribution ingredient is detailed and can carry out deposition on a high surface area support ingredient. A support ingredient is usually sunk into this using the precursor compound of a water-soluble high distribution ingredient. Subsequently, a precursor compound is converted into a high distribution ingredient by suitable temperature processing. The particle size of this high distribution ingredient is about 5-50nm.

[0029] A storage component means the element of alkali metal and alkaline earth metal within the limits of this invention. Advantageously, these are a potassium, a rubidium, caesium, magnesium, calcium, strontium, and barium. These form the oxide of the strong base nature which can combine nitrogen oxides. Therefore, the oxide of a storage component is also called a storage compound or an activity storage compound. However, as a concept of a storage compound, the resultant to a carbonate and a hydroxide with an oxide, air, and an exhaust gas component is also considered, and these can store nitrogen oxides similarly in this case. The storage capacity of a storage compound becomes so large that the basicity generally becomes strong.

[0030] A storage compound and a storage ingredient are distinguished. A storage ingredient is

the supported storage compound, i.e., the storage compound by which deposition was carried out on the suitable support ingredient in the form of high distribution. However, the storage compound which exists in a detailed form within the limits of this invention is also called a storage ingredient.

[0031] According to these breaks through of the used concept, this invention is explained below at a detail.

[0032] The catalyst by this invention has the second stratum functionale to which the hydrocarbon contained in Lean exhaust gas can also absorb catalytic activity on the primary-function layer which has the function to store nitrogen oxides. It is important for the function of the catalyst by this invention in that case that the support ingredient for a catalytic activity component is an acid support ingredient.

[0033] The acid suitable support ingredients for the catalytic activity component of the second stratum functionale are an aluminum silicate, a silicon dioxide, titanium oxide, and a zirconium dioxide. An aluminum oxide is seldom suitable as a support ingredient in the second stratum functionale the bisexual property and for [its] low acidity. The aluminum silicate of the silicon-dioxide content 1 - 40 mass % to the gross mass of an aluminum silicate is especially proved as a support ingredient for this invention. As a catalytic activity component, platinum and/or palladium are especially suitable. Only platinum is used advantageously.

[0034] For [for the consolidation of the acid property of the second stratum functionale] storage of a hydrocarbon, the zeolite of 20 or more modules (mole ratio to the aluminum oxide of a silicon dioxide) acid H-form is used.

[0035] The important thing for an operation of the catalyst by this invention is that concentration of the nitrogen oxides within a catalyst and a hydrocarbon is near the active center of a catalyst. This leads to remarkable activity lifting to a pure oxidation catalyst and a pure storage catalyst. The nitrogen-oxides storage ingredient in the first pass and the hydrocarbon storage ingredient in the second layer perform concentration. To a hydrocarbon, to about 200 degrees C and nitrogen oxides, the desorption temperature which can be measured macroscopically [both adsorption ingredients] is about 400 degrees C, and differs remarkably. However, the adsorption process and the desorption process have occurred regularly microscopically, and even the desorption temperature of 400 degrees C or less of the nitrogen oxides which can be measured macroscopically leads these to reduction of nitrogen oxides and coincidence at a catalytic activity core at isolation of a hydrocarbon, therefore clearance of the nitrogen oxides from adsorption / desorption balance.

[0036] If the above-mentioned process has exhaust gas temperature below in the macroscopic desorption temperature of nitrogen oxides, it will become advantageous. Although the compulsory heat desorption of the nitrogen oxides by the exhaust gas temperature of about 400 degrees C or more is not desirable, it is because hydrocarbons enough for it, that is, already [in this case] reduction cannot be used.

[0037] As for the latest direct injection diesel power plant, data with rare a heavy load also serving as exhaust gas temperature of 350-400 degrees C or more harmonize to this low temperature requirement. In the period of the great portion of operational status of these diesel power plants, the exhaust gas temperature is 400 degrees C or less. In a partial load field, these engines have the exhaust gas temperature of 100-250 degrees C. However, with the engine with which exhaust gas temperature is cooled suitably, even if it is the usual diesel power plant which has high exhaust gas temperature, if it arranges in the location in the exhaust gas equipment

which separated, the catalyst by this invention can be used.

[0038] The zeolite which has the mole ratio (module) of the silicon dioxide and aluminum oxide which exist in acid H-form and exceed 20 is used as independent or mixture to the second stratum functionale. They are dealumination-ized Y-zeolite, a zeolite ZSM5, or the dealumination-ized mordenite especially suitably.

[0039] The approach by this invention uses the microscopic adsorption process and desorption process of nitrogen oxides in low temperature. This behavior becomes advantageous by the activity of the nitrogen-oxides storage ingredient which carries out chisel association of the nitrogen oxides in adsorption.

[0040] Reversely, a different path from this was adopted with the well-known design for a nitrogen-oxides storage catalyst. These are substantially based on storing nitrogen oxides in the form of a nitrate by the reaction with a storage ingredient. There are two sorts of approaches for disassembly of this nitrate. As for one approach, an exhaust gas presentation is made as for a change to rich and a stoichiometry value from Lean. Under these exhaust gas conditions, a nitrate is 400 degrees C and is already disassembled. However, this approach does not benefit the fixed Lean air-fuel ratio of a diesel power plant a problem. Other approaches are possible pyrolyses under the Lean exhaust gas condition of a nitrate. However, for that, the temperature of 400 degrees C or more is required.

[0041] The catalyst by this invention mainly sticks to the great portion of nitrogen oxides as a nitrogen monoxide gently within a primary-function layer reversely. A prerequisite for this is that a little chisel oxidizes to a nitrogen dioxide very much in the case of the diffusion whose nitrogen oxides pass along the second up stratum functionale. The activity of the acid support ingredient for a catalytic activity platinum metal can attain this by this invention.

[0042] After exhaust gas diffuses the second stratum functionale, this reaches in the primary-function layer under it in the amount of the nitrogen dioxide which became high slightly. Here, chisel adsorption of the nitrogen monoxide contained in exhaust gas is carried out physically gently at a storage compound.

[0043] Thus, the second stratum functionale participates in combining nitrogen oxides gently in a primary-function layer substantially. Therefore, in all the conventional techniques, a well-known storage compound can be used as a nitrogen-oxides storage compound of a primary-function layer, namely, they are an alkali-metal oxide, an alkaline-earth-metal oxide, and the basic storage compound of a rare earth metal. Advantageously, a potassium, a rubidium, caesium, magnesium, calcium, strontium, and the storage compound of barium are used. Additionally, the primary-function layer can include manganese, cobalt, copper, zinc, tin, lead, the basic oxides of the transition metals from the group of a zirconium, or these combination.

[0044] However, loose association of the nitrogen oxides in a primary-function layer is supportable with suitable ingredient selection. It discovered beginning desorption to the extent that the storage compound which carried out deposition on the detailed support ingredient based on cerium oxide carries out chisel association of the nitrogen oxides gently and is accepted also at comparatively low exhaust gas temperature.

[0045] In this case, in 400 degrees C or less of important operating temperature, and certain Lean exhaust gas conditions, cerium oxide pure as a support ingredient, the doped cerium oxide, and a cerium / zirconium mixed oxide are suitable. The doped cerium oxide and the cerium / zirconium mixed oxide are always advantageous, also when an ingredient must be stabilized to the high exhaust gas temperature of 400 degrees C or more produced by chance thermally. That is, in high

exhaust gas temperature, a storage ingredient reacts to a support ingredient and a chemistry target, therefore there is risk of saying that the storage capacity is lost.

[0046] For thermal stabilization, cerium oxide can be stabilized by addition using the mixture of the oxide from the group which consists of silicon, a scandium, an yttrium, and a rare earth metal (a lanthanum, a praseodymium, neodymium, a promethium, samarium, a europium, a gadolinium, a terbium, a dysprosium, a holmium, an erbium, a thulium, an ytterbium, and lutetium), elements, or these oxides. for this reason, each oxide or the oxide mixture 0.5-20 -- 5 - 10 mass % is advantageously required. As opposed to the total mass of the cerium oxide which stabilized the publication of concentration in this case. addition -- the very thing -- a well-known approach, for example, coprecipitation, simultaneous heat hydrolysis, impregnation, and a deposit can perform.

[0047] In a commercial scene, it can obtain with the mixing ratio of extensive cerium oxide and a zirconium dioxide, and the cerium / JIRUKONIMU mixed oxide similarly used as a support ingredient for an advantageous storage compound have spread like pure cerium oxide as an oxygen storage ingredient in the 3 yuan storage ingredient of common use. Manufacture of a cerium / JIRUKONIMU mixed oxide can be performed with mechanical mixing or an impregnation method, and a coprecipitation method. The property which excelled within the limits of this invention in these ingredients is important as a support ingredient for a storage compound. The oxygen storage capacity is not so important.

[0048] The content of a cerium / JIRUKONIMU mixed oxide has an especially advantageous property as a support ingredient for a storage compound, when not exceeding 20 mass % to the total mass of a mixed oxide advantageously, the zirconium dioxide content 30 of a mixed oxide, and. However, in order to give good thermal stability to cerium oxide, the zirconium dioxide content of a mixed oxide must not be lower than 1 mass %. It is between the zirconium dioxide content 5 - 15 mass % especially advantageous. A remarkable good result can be obtained in zirconium dioxide content 10 mass %. Above zirconium dioxide content 30 mass %, cerium oxide cannot protect a zirconium dioxide from a reaction with a storage component in an elevated temperature. Therefore, the cerium / JIRUKONIMU mixed oxide which has zirconium dioxide 30 mass % are not suitable as a support ingredient for a storage compound under the service condition accompanied by high exhaust gas temperature.

[0049] With the combination of many descriptions by this invention, the above-mentioned catalyst has 20 - 30% of conversion rates of the nitrogen oxides in the oxygen content exhaust gas of the diesel power plant averaged over the run cycle of practical use. Therefore, this is substantially high to the conventional technique. Even if this conversion rate does not need to respond by the way and does not need to reproduce the storage compound in rich exhaust gas mixture, it is attained, namely, an engine can be continuously operated with Lean air / fuel mixture.

[0050] Furthermore, the combination by this invention shows the good conversion with remarkable carbon monoxide, hydrocarbon, and particulate matter other than the comparatively high nitrogen-oxides conversion rate which a 120-400-degree C remarkable low operating temperature is the description, and was observed.

[0051] Other advantages of a catalyst are the high resistance over poisoning of the storage compound by the sulfur oxide. This poisoning resistance is based on the acid ingredient of the second stratum functionale which controls oxidization of the sulfur dioxide contained in exhaust gas, and forms a diffusion barrier.

[0052] The following drawing explains this invention to a detail further.

[0053] Drawing 1 : the lamination of the catalyst by this invention.

[0054] Drawing 2 : the nitrogen-dioxide formation by the catalyst of the second stratum functionale.

[0055] The stratum functionale of both catalysts is used by drawing 1 on the inert carrier. As support, a well-known ceramic or a metaled honeycomb object is used, and these have the passage for much exhaust gas in the cross section. A coat is used on the wall surface of passage by the well-known approach. The cel consistency of this honeycomb object, i.e., the number of passes per cross section, can be 10-200cm⁻².

[0056] The coat concentration of all coats is 100 - 400 g/l (honeycomb object volume) advantageously. The rate of the second stratum functionale to all coats is made into ten to 50 mass % in that case. If the rate of the second stratum functionale exceeds 50 mass %, diffusion of the nitrogen oxides to the storage compound of the first pass will worsen with steps through this layer. If the rate of the second stratum functionale becomes below 10 mass %, it runs short, in order for the storage capacity to a hydrocarbon to prepare hydrocarbons enough for reduction of the after that of the nitrogen oxides which separated.

[0057] Because of the catalytic activity of the covered catalyst object, the geometric array on a catalyst object other than the total mass of the catalytic activity matter is important. Generally the catalytic activity of the catalyst in the amount of coats given beforehand has a high direction in the case of using the coat on large geometric surface area. Larger geometric surface area can be based on the large volume of a catalyst object, or can be obtained with a high cel consistency. A ratio [as opposed to the volume VKat of the geometric surface area OKat to the case of the usual ceramic support for the usual catalyst which has cel consistency 62cm⁻²] is about 2.4m²/l.

[0058] The ratio to the cubic capacity VHub of the diesel power plant of the geometric surface area must have 1-10m²/l to the catalyst by this invention. Generally the value below 1m²/l gives inadequate catalytic activity. An increment of the ratio to the cubic capacity VHub of geometric catalyst surface area improves emission gas purification. However, the improvement which can reach will decrease, if a ratio becomes large. Therefore, above 10m²/[of ratios] 1, it is spatially meaningless also in cost.

[0059]

[Example] It is used on the open cel support which consists the following dimension of the cordierite which it has in the following catalysts and comparison catalysts according [on an example and] to this invention.

[0060]

A diameter 14.37 cm die length 15.24 cm cel consistency 62 cm⁻² wall thickness 0.2 mm volume 2.5 l geometric surface area 6 In m² preliminary-experiment preliminary experiment, the oxidation to the nitrogen dioxide of a nitrogen monoxide was examined about combination of the catalyst for the second stratum functionale. For this reason, three honeycomb objects which have the following catalyst combination were covered.

[0061] first catalyst: -- 100g/l.gamma-aluminum2O3+3.5g/lPt; -- an aluminum oxide has specific-surface-area of 140m²/g. Before the coat of this of a honeycomb object, the platinum-salts solution was used and it sank in, and it calcinated in 300 degrees C for 4 hours.

[0062] The second catalyst: Aluminum-oxide 100 g/l which added silicon (2 SiO5 mass %, 2O3 aluminum95 mass %, 150m²/g). Manufacture was performed like the first catalyst.

[0063] The third catalyst: Aluminum-oxide 100 g/l which added silicon (2 SiO40 mass %, 2O3

aluminum 40 mass %, 150 m²/g). Manufacture was performed like the first catalyst.

[0064] From three sorts of catalysts, the hole was opened, the specimen was extracted and the load of the synthetic exhaust gas mixture of the following presentation was carried out within synthetic gas equipment.

[0065]

Nitrogen monoxide : 270 volume ppm propene : 90 volume ppm carbon monoxide : 350 volume ppm hydrogen : 116 volume ppm sulfur dioxide : 20 volume ppm oxygen : 6 volume % steam: 10 volume % carbon dioxide: 10 volume % nitrogen: It flowed through the residue gaseous mixture in the specimen in space-velocity 100000 h⁻¹, and heated from a room temperature to 500 degrees C by part for 15-degree-C/in rate. The formed nitrogen-dioxide concentration was measured in the back of a specimen.

[0066] Drawing 2 shows the obtained measurement curve. Below 200 degrees C, a nitrogen monoxide passes a catalyst, without oxidizing to a nitrogen dioxide. In about 210 degrees C or more, the first catalyst which has gamma-aluminum oxide pure as a support ingredient to Pt starts formation of a nitrogen dioxide.

[0067] The second catalyst using the aluminum oxide which added silicon 5 mass % as a support ingredient had the inclination of low nitrogen-dioxide formation substantially. This can ask the high acidity of this support ingredient for a cause. Reduction beyond this of formation of a nitrogen dioxide is accepted in the third catalyst, and the support ingredient is acidity more nearly further than the support ingredient of the second catalyst because of the content of silicon-dioxide 40 mass %.

[0068] Therefore, an aluminum oxide pure for the object of this invention has low fitness as a support ingredient for the catalytic activity component of the second stratum functionale. The acid support ingredient of the second and third catalysts is more suitable. These are led to the low oxidation of platinum to a nitrogen monoxide. Thus, the nitrogen monoxide contained in exhaust gas can be passed without changing in most of the second stratum functionale. Subsequently to in a primary-function layer, this is combined by physical adsorption.

[0069] The example 1 of a comparison: The reduction catalyst was manufactured as follows like Example 1 out of the German (patent DE) No. 19614540A1 description.

[0070] The aluminum silicate (specific-surface-area: 286 m²/g measured by DIN 66132) containing silicon-dioxide 5 mass % was activated using platinum. For this reason, when the aluminum silicate was contacted continuing the water solution of a tetra-ammine platinum (II) hydroxide, and stirring, the damp fluid powder generated it. The powder generated after drying in 120 degrees C and air for 12 hours was calcinated in air in 300 degrees C for 2 hours. Powder was succeedingly returned in 500 degrees C for 2 hours in the circulating foaming gas (Formiargas) (2 N₉₅ volume % and 2 H₅ volume %). Thus, the manufactured platinum / aluminum-silicate-powder contained platinum 3.4 mass % to total mass.

[0071] the coat which has solid-state content 40 mass % from the platinum / aluminum-silicate-powder which carried out preliminary manufacture -- service water -- sex dispersion liquid were manufactured. The following zeolite powder was added to these dispersion liquid by the ratio 1:1:1:1:1.

[0072] DAY (x= 200), Na-ZSM -5 (x> 1000), H-ZSM -5 (x= 120), H-ZSM -5 (x= 40), and H-mordenite (x= 20).

[0073] It was immersed into these dispersion liquid for a coat, and the above-mentioned honeycomb object was covered. The enveloping layer was dried in air in 120 degrees C, and it

calcinated at 500 degrees C succeedingly for 2 hours. The completed catalyst contained 140g of oxides, and 3.18g of platinum per catalyst volume liter.

[0074] The exact presentation of the completed coat is indicated to a table 1. The relative array between both various components is given below.

[0075]

[Formula 1]

Si/Al ₂ O ₃	+ Pt	}	全被覆層
H- モルデン沸石	(x=20)		
H-2SM5	(x=40)		
H-2SM5	(x=120)		
H-2SM5	(x>1000)		
DAY	(x=200)		

[0076] The nitrogen-oxides storage catalyst on an example of comparison 2 honeycomb object was manufactured as follows.

[0077] The aluminum oxide (specific surface area: 134m²/g) was activated using platinum and palladium. For this reason, when it was made to contact, continuing the water solution and stirring which consist an aluminum oxide of a tetra-ammine platinum (II) nitrate and a palladium nitrate (II), damp platinum / palladium-aluminum oxide-powder which all contains platinum content 1.23 mass % and palladium content 0.71 mass % to an aluminum oxide generated. After drying in 120 degrees C and air for 2 hours, powder was calcinated in air in 300 degrees C for further 2 hours, and it returned at 500 degrees C succeedingly for 2 hours among the circulating foaming gas.

[0078] Furthermore, the cerium / zirconium-mixed oxide (cerium oxide 70 mass %; zirconium dioxide 30 mass %; specific surface area : 104m²/g) was sunk in using the rhodium. For this reason, in the pH value 6, the mixed oxide dispersion liquid of solid-state content 40 mass % were added in 15 minutes, continuing and stirring a nitric-acid rhodium (III) solution. These dispersion liquid were carried out the ** exception in 15 more minutes. It dried in air at 120 degrees C, and the solid-state was calcinated in 300 degrees C and air for 4 hours for 2 hours. The rhodium-cerium / zirconium mixed oxide powder manufactured by this approach had rhodium content 1.59 mass % to the cerium / zirconium-mixed oxide.

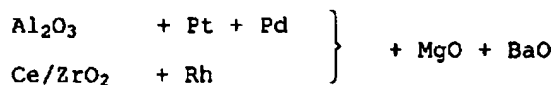
[0079] the coat of solid-state content 40 mass [from powder] % in which both carried out preliminary manufacture -- service water -- sex dispersion liquid were manufactured. It added and the magnesium acetate which is equivalent to magnesium-oxide ratio 7.85 mass % to a total solid-state content was added.

[0080] It was immersed into these coat dispersion liquid, and the honeycomb object was covered. It dried in 120 degrees C and air, and the enveloping layer was succeedingly calcinated in 500 degrees C for 2 hours. Then, it sank in using the barium acetate water solution, and dried within the oven in 120 degrees C for 2 hours anew, and the covered honeycomb object was succeedingly calcinated at 500 degrees C for 2 hours.

[0081] The exact presentation of the completed coat is indicated to a table 1. The relative array between both various components is given below.

[0082]

[Formula 2]



[0083] The catalyst by this invention which has example 1 stratum-functionale two-layer was manufactured.

[0084] As a primary-function layer, the storage catalyst of the example 2 of a comparison was used. The oxide content decreased 0.78 times proportionally compared with the example 2 of a comparison. The enveloping layer was dried in air in 120 degrees C, and it calcinated in 500 degrees C for 2 hours succeedingly.

[0085] As the second stratum functionale, the reduction catalyst of the example 1 of a comparison was used. The oxide content decreased 0.71 times proportionally compared with the example 1 of a comparison. The platinum load of the second stratum functionale was 3.18 g/l. The enveloping layer was dried in 120 degrees C and air, and it calcinated in 300 degrees C for 4 hours, and returned in 500 degrees C and foaming gas succeedingly for 2 hours.

[0086] Example 2: the catalyst by another this invention was manufactured.

[0087] As a primary-function layer, the storage catalyst of the example 2 of a comparison was used. The oxide content decreased 0.78 times proportionally compared with the example 2 of a comparison. The coat was dried in air in 120 degrees C, and it calcinated in 500 degrees C for 2 hours succeedingly.

[0088] The second stratum functionale was manufactured as follows.

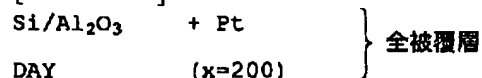
[0089] The solids-mixing object which consists of aluminum-silicate (silicon-dioxide 5 mass %, specific-surface-area:147m2/g) 85 mass % and dealuminization-ized zeolite Y(x= 200)15 mass % was activated using platinum. For this reason, when the solids-mixing object was contacted continuing the water solution of an ethanolamine platinum (IV) hydroxide, and stirring, the damp fluid powder generated it. The powder generated after drying in 120 degrees C and air for 12 hours was calcinated in air in 300 degrees C for 4 hours, and it returned in foaming gas in 500 degrees C for 2 hours. Thus, the powder mixture activated using platinum contained platinum 2.65 mass % to the mass of an aluminum silicate.

[0090] this powder -- using -- the coat of solid-state content 40 mass % -- service water -- sex dispersion liquid were manufactured. It was immersed into these coat dispersion liquid, and the honeycomb object was covered. The enveloping layer was dried in 120 degrees C and air, and it calcinated in 300 degrees C for 4 hours, and returned in foaming gas in 500 degrees C for 2 hours succeedingly. The presentation of the acquired catalyst is indicated to a table 1.

[0091] The relative configuration between the components of the versatility of the second stratum functionale is expressed with the following formula.

[0092]

[Formula 3]



[0093] Although powder mixture sank in the whole using platinum, most only carried out the deposition of the platinum on the aluminum silicate.

[0094] Example 3 -- the catalyst by another this invention was manufactured. The primary-function layer was manufactured as follows.

[0095] It is zirconium dioxide powder (specific surface area: 103m2/g) CeO2 10.64 mass %, La

2O3 It sank in using 9.50 mass % and Pd3.8 mass %. For this reason, when it was used continuing stirring on a zirconium dioxide with the mass ratio which corresponds the water solution which consists of a cerium nitrate (III), a lanthanum nitrate (III), and a palladium nitrate (II), the zirconium dioxide powder by which impregnation was become wet and carried out generated. The generated powder was calcinated in 600 degrees C and air after desiccation in 150 degrees C and air for 2 hours for 2 hours.

[0096] the coat which has solid-state content 40 mass % using the zirconium dioxide powder which sank in, an aluminum oxide (specific surface area: 134m2/g), and a cerium / zirconium mixed oxide (70/30; surface area : 104m2/g) -- service water -- sex dispersion liquid were manufactured. The rate of zirconium dioxide powder to a coat dispersion-liquid dry mass was [57.64 mass %, and the cerium / zirconium mixed oxide of 18.94 mass % and an aluminum oxide] 10.80 mass %s. It added and the barium acetate which is equivalent to dispersion liquid at barium-oxide 12.62 mass % was added.

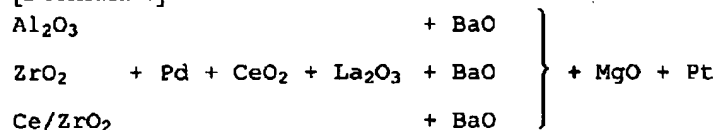
[0097] Like the above-mentioned example, the honeycomb object was covered using these dispersion liquid for a coat, it dried in 120 degrees C and the coat was succeedingly calcinated in 500 degrees C for 2 hours.

[0098] Then, it sank in using the solution which consists of the magnesium nitrate and tetra-amine platinum (II) nitrate equivalent to magnesium-oxide 9.1 g/l and platinum 3 g/l, and dried in 120 degrees C, and the covered honeycomb object was calcinated for 2 hours. The second stratum functionale of Example 2 was used as the second stratum functionale. The presentation of the completed catalyst coat is indicated to a table 1.

[0099] The mutual relative configuration of the various components of a primary-function layer is expressed with the following formula.

[0100]

[Formula 4]



[0101] Example 4: the catalyst by another this invention was manufactured. The primary-function layer was manufactured as follows.

[0102] The coat was manufactured using three sorts of different oxide powder. Three sorts of powder is the following.

[0103] - Powder 1 : cerium oxide which sank in using the cerium / zirconium mixed oxide, and the powder 3:barium oxide which sank in using the aluminum oxide and the powder 2:rhodium which sank in using platinum.

[0104] Manufacture of these three sorts of powder was performed as follows.

[0105] Powder 1: If an aluminum oxide (specific surface area: 134m2/g) is contacted to an ethanolamine platinum (IV) hydroxide, continuing stirring, the damp fluid powder will generate it. The powder generated after ***** was calcinated in 300 degrees C and air in 120 degrees C and air for 2 hours for 12 hours. Then, in 500 degrees C, it returned under foaming gas for 2 hours. Thus, the manufactured platinum/aluminum oxide dust contained platinum 3.5 mass % to the aluminum oxide.

[0106] Powder 2: The 40 mass % dispersion liquid of a cerium / zirconium mixed oxide (70/30;104m2/g) were manufactured. In the pH value 6, stirring mixing of the nitric-acid

rhodium (III) solution was carried out in 15 minutes into these dispersion liquid. Dispersion liquid were carried out the ** exception in 15 more minutes. It dried in 120 degrees C and air, and the solid-state was calcinated in 300 degrees C and air for 4 hours for 2 hours. Thus, the manufactured rhodium-cerium / zirconium mixed oxide powder had rhodium content 1.59 mass % to the mixed oxide.

[0107] Powder 3: When sunk in using the barium acetate water solution (barium-oxide 15.48 mass %), continuing stirring, it became wet and fluid powder generated cerium oxide (specific surface area: 104m2/g). After drying in 120 degrees C and air for 12 hours, powder was calcinated in 500 degrees C and air for 2 hours.

[0108] the coat of solid-state content 40 mass [from three sorts of powder] % -- service water -- sex dispersion liquid were manufactured. The rate of the powder 1 of a dry substance was [8.6 mass % and the powder 3 of 40.50 mass % and powder 2] 50.9 mass %s.

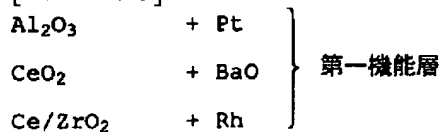
[0109] The honeycomb object was covered using these dispersion liquid for a coat. The enveloping layer was dried in air in 120 degrees C, and it calcinated in 500 degrees C for 2 hours succeedingly.

[0110] As the second stratum functionale, the second stratum functionale of Example 2 was used like Example 3 of the first half. The exact presentation of the completed coat is indicated to a table 1.

[0111] The mutual relative configuration of the various components of a primary-function layer is expressed with the following formula.

[0112]

[Formula 5]



[0113]

[A table 1]

表 1 : 触媒の組成

原 料 第二機能層	比較例 1 [g/l]	比較例 2 [g/l]	例 1	例 2 [g/l]	例 3 [g/l]	例 4 [g/l]
ケイ酸アルミニウム	93.5	---	66.4	85.2	85.2	85.2
H-モルデン沸石 (x = 20)	9.3	---	6.6	---	---	---
H-ZSM5 (x = 40)	9.3	---	6.6	---	---	---
H-ZSM5 (x = 120)	9.3	---	6.6	---	---	---
H-ZSM5 (x > 1000)	9.3	---	6.6	---	---	---
DAY (x = 200)	9.3	---	6.6	14.2	14.2	14.2
酸化物含有量	140	---	99.4	99.4	99.4	99.4
白金 第一機能層	3.18	---	3.18	3.18	3.18	3.18
酸化アルミニウム	---	174	135.7	135.7	107.2	78
酸化ジルコニウム	---	---	---	---	26.8	---
酸化セリウム	---	---	---	---	3.8	85.8
セリウム/ジルコニウム混合酸化物	---	22	17.2	17.2	20.1	16.9
酸化ランタン	---	---	---	---	3.4	---
酸化バリウム	---	35	27.3	27.3	23.5	15.6
酸化マグネシウム	---	20	15.6	15.6	6.1	---
酸化物含有量	---	251	195.8	195.8	190.9	196.3
白金	---	2.14	2.14	2.14	3	3.5
パラジウム	---	1.23	1.23	1.23	2	---
ロジウム	---	0.35	0.35	0.35	---	0.35
全被覆						

[0114] The catalytic activity of the emission-gas-purification catalyst of the example of activity 1 above-mentioned example was measured in synthetic gas equipment. If this equipment is used, it is possible to copy and form all the gas-like exhaust gas components that exist in the actual exhaust gas of a diesel power plant or an Otto engine. The test condition and model gas presentation which were selected are displayed on a table 2.

[0115] As a specimen, the well core of the ****ing catalyst with a diameter [of 25mm] and a die length of 76mm was selected. The specimen was divided into one half in order to maintain uniformly the catalyst volume used for the trial, in connecting two sorts of specimens approximately.

[0116] The measuring device of table 3 publication was used for the gas-constituents measurement included in exhaust gas.

[0117] For the initiation thermometry, exhaust gas was heated by part for heating rate/of 15 degrees C. In 400 degrees C, condition adjustment of the specimen was first carried out for 1 hour in the exhaust gas mixture of table 6 publication. The catalytic activity which the combination of the selected catalyst measured is indicated to a table 4.

[0118]

[A table 2]

表2：合成気体装置内における有害物質CO、HCおよびNO_xの変換率の測定のための試験条件およびモデルガス組成

成分	濃度
CO	350〔容積PPM〕
H ₂	117〔容積PPM〕
HC ₁ *	270〔ppmC ₁ 〕
SO ₂	20〔容積PPM〕
NO	270〔容積PPM〕
O ₂	10〔容積%〕
H ₂ O	10〔容積%〕
CO ₂	10〔容積%〕
N ₂	残量
全量	1950〔Nl/時間〕
触媒の大きさ	直径25mm × 76mm
空間速度	50000〔時間 ⁻¹ 〕
加熱速度	15〔℃/分〕

HC₁*：炭化水素成分として、プロペンとプロパンのモル比1：1から成る混合物を使用した。表5の記載数字は、炭素原子1個に対するものである。

[0119]

[A table 3]

表3：合成気体試験状態の排ガス濃度の測定のための測定装置の構成

分析する気体	測定装置	製造者
O ₂	オキシマート	ジーメンス株式会社
炭化水素	FID	ピールブルク・メステヒニク
NO _x	CLD700Elht	ツェルヴェーゲル・エコシステム
CO	Binos	ローズマウント
CO ₂	Binos	ローズマウント
SO ₂	Binos	ローズマウント

[0120]

[A table 4]

表4：合成気体内の400℃における1時間条件調整後の触媒の有害物質変換

例	NO _x 温度 範囲 ¹⁾ 〔℃〕	最高NO _x 変換温度 〔℃〕	最高NO _x 変換率 〔%〕	T _{50,CO} ²⁾ 〔℃〕	T _{50,HC} ³⁾ 〔℃〕
比較例1	190-220	200	30	135	165
比較例2	180-220	205	35	185	198
例1	161-242	193	52	152	178
例2	165-245	194	53	150	173
例3	167-250	195	57	148	176
例4	160-270	180	60	144	174

1) 貴金属ベースの触媒は、窒素酸化物が変換される一定の温度範囲を有する。この範囲を温度範囲(Temperaturefenster)と呼ぶ。この使用例における温度範囲は、NO_x変換20%が起きる温度範囲と定義する。

2) CO変換50%に達する温度

3) HC変換50%に達する温度

[0121] The catalytic activity of the catalyst selected example of activity 2 was added, and it examined in the car. As a trial car, the 1.9L diesel power plant and the passenger car with an output of 81kW were used. The car roll trial was performed using the diesel fuel of marketing below the sulfur content 500 mass ppm specified to Euro2 specification. The instrument for analysis used for measurement of harmful matter blowdown is the same as the thing of example of activity 1 publication (table 3 reference).

[0122] The result of this trial after the catalyst aging in the exhaust gas temperature of 350 degrees C is displayed on a table 5 for 6 hours. The catalyst by this invention by Example 3 showed 25% of reduction to the unsettled excretions in the train of "having no catalyst", and, on the other hand, the catalyst of the examples VB1 and VB2 of a comparison fell only about 13% to unsettled excretions.

[0123]

[A table 5]

表5：1.9 Lディーゼルエンジンを有する乗用車で350℃において触媒の6時間エンジン老化の後のMVEG-A試験サイクルにおける有害物質排出

例	O_{Kat}/V_{Hub} (m^2/l)	MVEG-A試験サイクルにおける排出物 (g/km)			
		NO_x	CO	HC	粒状物質
触媒なし		0.69	0.72	0.15	0.058
比較例1	6.32	0.62	0.13	0.02	0.038
比較例2	6.32	0.60	0.43	0.08	0.050
例3	6.32	0.52	0.07	0.02	0.038

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The lamination of the catalyst by this invention is expressed.

[Drawing 2] The nitrogen-dioxide formation by the catalyst of the second stratum functionale is expressed.

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.